



Synthesis and Applications of Non-spherical Dimer Colloids

Citation

Yoon, Kisun. 2012. Synthesis and Applications of Non-spherical Dimer Colloids. Doctoral dissertation, Harvard University.

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Dissertation advisor:
Professor David A. Weitz

Author:
Kisun Yoon

Synthesis and Application of Non-spherical Dimer Colloids

Abstract

Colloids are promising building blocks in material synthesis because of their controllability of size and surface properties. The synthesis of chemically and/or geometrically anisotropic colloidal particles has received attentions with the expectation of building blocks for complex structures. However, the synthesis of anisotropic colloidal particles is by far more difficult than the synthesis of spherical colloidal particles. Lack of monodispersity and productivity of many anisotropic particles often limits their applications as a building block for complex structures. Thus, it is highly desirable to develop methods which can produce a large amount of monodisperse non-spherical particles with controllable asymmetric surface properties. This dissertation details the work for developing such a method.

The major result of this dissertation is a synthetic method to produce monodisperse non-spherical colloids with anisotropic surface property in a large quantity. The anisotropic colloid, which we call it as Dimer particle, has two fused lobes like a dumbbell and each lobe's size can be independently controlled. We present a novel method to synthesize sub-micron size Dimer particles. This method can produce a large amount of submicron-sized Dimer particles with good monodispersity and well-controlled shape. Submicron-sized Dimer particles have been highly desired since they can be used as a building block for self assembly using Brownian motion, colloidal surfactant for Pickering emulsion, and photonic materials.

To fully take advantage of the anisotropy of the particles, we develop a facile method to tailor the surface property of each lobe independently by asymmetrically coating the particles with gold nanoparticles. This method doesn't need the arrangement of particles onto any type of interfaces. Asymmetric coating of gold nanoparticles can be carried out simply by mixing Dimer particles with gold nanoparticles. The formation mechanism of the submicron-sized Dimer particles is explained with evidences.

Finally, we illustrate that Dimer particles show rich phase behavior under electric fields and explain the behavior by considering various interactions involved in the system. Our investigation shows that electric field can effectively control the orientation and

assembled structure of Dimer particles. In conclusion, these asymmetrically functionalized Dimer particles are promising building blocks to generate suprastructures that will be useful in photonic, electronic and diagnostic applications.

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Citations to Previously Published Work

Chapter 2 and 3 appeared in its entirety as

“Asymmetric functionalization of colloidal dimer particles with gold nanoparticles”,

Kisun Yoon, Daeyeon Lee, Jin-Woong Kim, Jaeyun Kim, and David A. Weitz,

ChemComm (Accepted in May 2012)

Acknowledgement

I thank Dave Weitz, my advisor, for giving me the wonderful opportunity to learn how to conduct scientific research and generously allowing me to spend quite amount of time in studying quantitative finance along with my Ph.D. research.

I thank Daeyeon Lee, my mentor, for setting me down in this research when I didn't know what research I should do for my Ph.D. I thank Jin Woong Kim for his pioneering work in Dimer particle synthesis and sharing his valuable experiences with me. I thank Ning Wu for analyzing the behavior of Dimer particles in electric fields.

I thank Jonga Hur, my wife, for her dedicated support throughout my Ph.D. study.

Chapter 1

Introduction: anisotropic colloids

Colloid is a micron-sized dispersed phase in a continuous media.(Russel, Saville et al. 1989) The examples of colloids include milk, paint, mayonnaise, and polystyrene particles dispersed in water. The typical size of the colloid particles is around one micron and it is about 1% of the thickness of human hair. Colloid particles are large enough that their dynamics can be investigated by an optical microscope and small enough that their dynamics are driven by Brownian motion.

One of the major breakthroughs in colloid science is the invention of synthetic methods that produce monodisperse colloid particles.(Sugimoto 1987; Bosma, Pathmamanoharan et al. 2002) Monodisperse colloids have been playing an important role in understanding the physics of colloids.(Kegel and van Blaaderen 2000; Schall, Cohen et al. 2004; Schall, Weitz et al. 2007) In addition, monodisperse colloids have received attentions in recent years as a building block for fabricating complex functional materials.(van Blaaderen 2003; Glotzer 2004; Perro, Reculosa et al. 2005; Glotzer and Solomon 2007) The fabrication of complex functional materials using colloidal particles

typically involves organization of particles into crystals, patterns or more complex phases. Since spherical isotropic particles can be arranged only to simple crystal structures such as Face Centered Cubic (FCC), researchers started considering anisotropic colloid particles to achieve more complex structures. Anisotropic colloid particles refer to colloids having anisotropic shapes and/or surface properties.

Vast amount of researches has been conducted to introduce anisotropy into colloidal building blocks with the goal of attaining complex structures. For example, stamping,(Cayre, Paunov et al. 2003; Cayre, Paunov et al. 2003; Paunov and Cayre 2004) controlled nucleation followed by precipitation,(Sugimoto, Itoh et al. 1997; Yu, Chen et al. 2005) microfluidics,(Xu, Nie et al. 2005; Dendukuri, Pregibon et al. 2006) and clusterization(Bosma, Pathmamanoharan et al. 2002; Manoharan, Elsesser et al. 2003; Yi, Manoharan et al. 2004; Cho, Yi et al. 2005) have been used to produce anisotropic particles. However, anisotropic colloidal particles synthesized in laboratories have little impact on practical industries mainly because most methods can produce the anisotropic colloids only in a milligram scale and it is difficult to scale up the production methods.(Perro, Meunier et al. 2009)

The major result of this dissertation is the development of a synthetic method to produce scalable monodisperse non-spherical colloids with anisotropic surface property.

The anisotropic colloid, which we call it as Dimer particle, has two fused lobes like a dumbbell and each lobe's size can be independently controlled. Dimer particles with high uniformity in size and shape can be produced in a large quantity (~ grams) using a synthetic technique called seeded-emulsion polymerization. These dimer particles can be used as building blocks to fabricate new photonic materials,(Hosein and Liddell 2007; Hosein, Ghebrebrhan et al. 2009; Forster, Park et al. 2011) and other complex structures.(Kraft, Vlug et al. 2008; Kraft, Groenewold et al. 2009; Park, Forster et al. 2009) They also can be studied as colloid surfactant for the stabilization of pickering emulsions.(Kim, Lee et al. 2008)

In chapter 2, we present a novel method to synthesize submicron-sized Dimer particles. This method can produce submicron-sized Dimer particles with good monodispersity and well-controlled shape. Submicron-sized Dimer particles have been highly desired since they can be used as a building block for self assembly using Brownian motion.(Mock, De Bruyn et al. 2006)

Chapter 3 illustrates asymmetric functionalization of Dimer particles with gold nanoparticles. We develop a method to tailor the surface property of each lobe independently by asymmetrically coat the particles with gold nanoparticles for achieving anisotropy. This method doesn't need the arrangement of particles onto any type of

interfaces. Asymmetric coating of gold nanoparticles can be carried out simply by mixing Dimer particles with gold nanoparticles. The formation mechanism of the submicron-sized Dimer particles is explained with evidences.

Chapter 4 illustrate that Dimer particles show rich phase behavior under electric fields and explain the behavior by considering various interactions involved in the system. Our investigation shows that electric field can effectively control the orientation and assembled structure of Dimer particles. In particular, we obtain close-packed crystals of standing Dimer particles. This assembly is of interest in fabricating 3D photonic crystals.(Xia, Gates et al. 2000)

The synthetic method to produce submicron-sized Dimer particles has been actively taught to material scientists and physicists who are interested in exploiting them in their researches. We have been witnessing many research progresses done by our colleagues who learned how to synthesize the Dimer particles from us. Asymmetrically functionalized Dimer particles are expected to generate complex functional materials that will be useful in photonic, electronic and diagnostic applications(Fudouzi and Xia 2003; Yoshida and Lahann 2008) and it is exciting to observe how the applications of our synthetic technology are evolving in various research fields.

Chapter 2

Synthesis of submicron-sized Dimer particles using seeded-emulsion polymerization

2.1 Introduction

Colloids are promising building blocks in material synthesis because of their controllability of surface properties and capability of being produced in large amount.(Glotzer 2004) However, spherical isotropic colloids have shown their limits as a building block in attaining complex structures. For example, crystallizing spherical colloids result in only limited sorts of ordered structures such as face-centered cubic or hexagonal close-packed.(Xia, Gates et al. 2000) Consequently, the synthesis of chemically and/or geometrically anisotropic colloidal particles has received attentions with the expectation of expanding the intricacy of the self-assembled structures.(Perro, Reculosa et al. 2005; Glotzer and Solomon 2007; Solomon, Zeitoun et al. 2010)

The fabrication of anisotropic colloidal particles suited for material synthesis is, however, by far more difficult than the fabrication of spherical colloidal particles. Lack

of monodispersity and productivity of many anisotropic particles often limits their applications as a building block for complex structures. One of the simplest forms of anisotropic colloidal particles is Janus particle. Janus Particles refer to spherical particles having two different types of surfaces.(Perro, Reculosa et al. 2005) Although Janus particles are the least complicated anisotropic particles we can imagine, most methods to produce Janus particles show difficulties in producing the particles in a large quantity. For example, synthesis of asymmetrically gold-coated Janus particles typically adopts arraying colloidal particles at an interface, which is then followed by the deposition of gold.(Paunov and Cayre 2004; Cui and Kretzschmar 2006; Suzuki and Kawaguchi 2006) This approach requires 2D alignment of particles and, consequently, and it is difficult to scale up the production. Only a few milligrams of Janus particles can be produced in a single batch.

Dimer particles are anisotropic polystyrene colloidal particles with two partially fused spherical lobes (Figure 2.1). The original goal of Dimer particle synthesis was to study polymer physics of Interpenetrating Polymer Networks.(Sheu, Elaasser et al. 1990) With the growing interests in synthesis and applications of anisotropic colloids, Dimer particle has received attentions since they are anisotropic colloidal particles which can be produced in a large amount while maintaining monodispersity. Researches on Dimer

particle synthesis have been conducted to better control the shape,(Kim, Larsen et al. 2006) use them as a precursor for more complex structures,(Kim, Larsen et al. 2007; Kraft, Vlug et al. 2008; Kraft, Groenewold et al. 2009) and impart chemical anisotropy by additional functionalizations.(Kim, Lee et al. 2008)

Seeded-emulsion polymerization is exploited to synthesize monodisperse Dimer particles; swelling cross-linked particles with monomer, heating the swollen particles to increase the elastic stress of the cross-linked network, and eventually causing the extrusion of monomer out of the network.(Sheu, Elaasser et al. 1990; Sheu, Elaasser et al. 1990; Kim, Larsen et al. 2006) This synthetic method works well to make Dimer particles whose size is a few microns. However, it turns out to be difficult for the conventional method to synthesize submicron-sized Dimer particles because the increasing effect of surface tension with smaller diameter forces the particles to maintain spherical shape.(Mock, De Bruyn et al. 2006) Submicron-sized Dimer particles are highly desired since they can be used as a building block for self assembly using Brownian motion,(Solomon, Zeitoun et al. 2010) colloidal surfactant for Pickering emulsion,(Binks and Fletcher 2001) and photonic materials.(Zhang, Keys et al. 2005) Herein, we present a facile method to synthesize sub-micron size Dimer particles by modifying the surface of

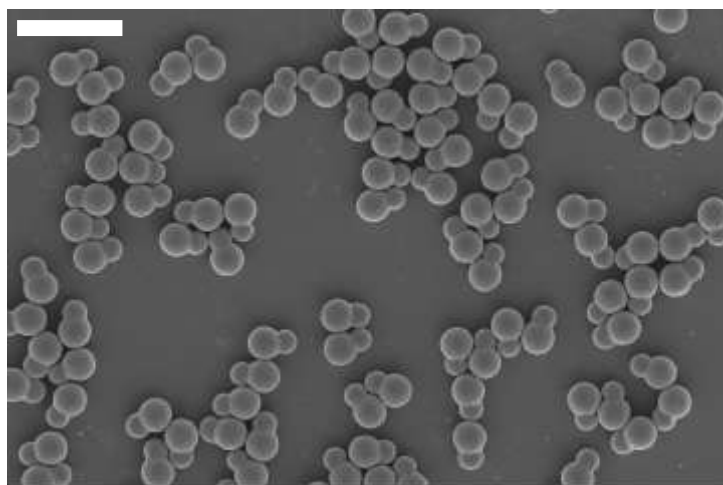


Figure 2.1: SEM image of Dimer particles. The scale bar represents 10 μ m.

seed particles using a silane-coupling agent. This method can produce a large amount of submicron-sized Dimer particles with good monodispersity and well-controlled shape.

2.2 Results and Discussion

Seeded-emulsion polymerization consists of swelling seed particles with monomer and then raising the temperature for free radical polymerization (Figure 2.2). Dimer particles have been synthesized by conducting two consecutive seeded-emulsion polymerizations.(Kim, Larsen et al. 2006) Spherical cross-linked particles are made by the first seeded-emulsion polymerization (Figure 2.3a). The spherical cross-linked particles are then transformed into Dimer particles by the second seeded-emulsion polymerization. During the second seeded-emulsion polymerization, the swollen monomer phase-separate from the cross-linked particle due to the increased elastic stress upon heating (Figure 2.3b).(Kim, Larsen et al. 2006) The elastic stress originates from the seed particle's cross-linked network. However, this synthetic approach doesn't work to synthesize submicron-sized Dimer particles. If seed particles are smaller than one micron, the elastic stress from the cross-linked network no longer provides enough free energy gain to overcome the free energy loss from the increased interfaces.

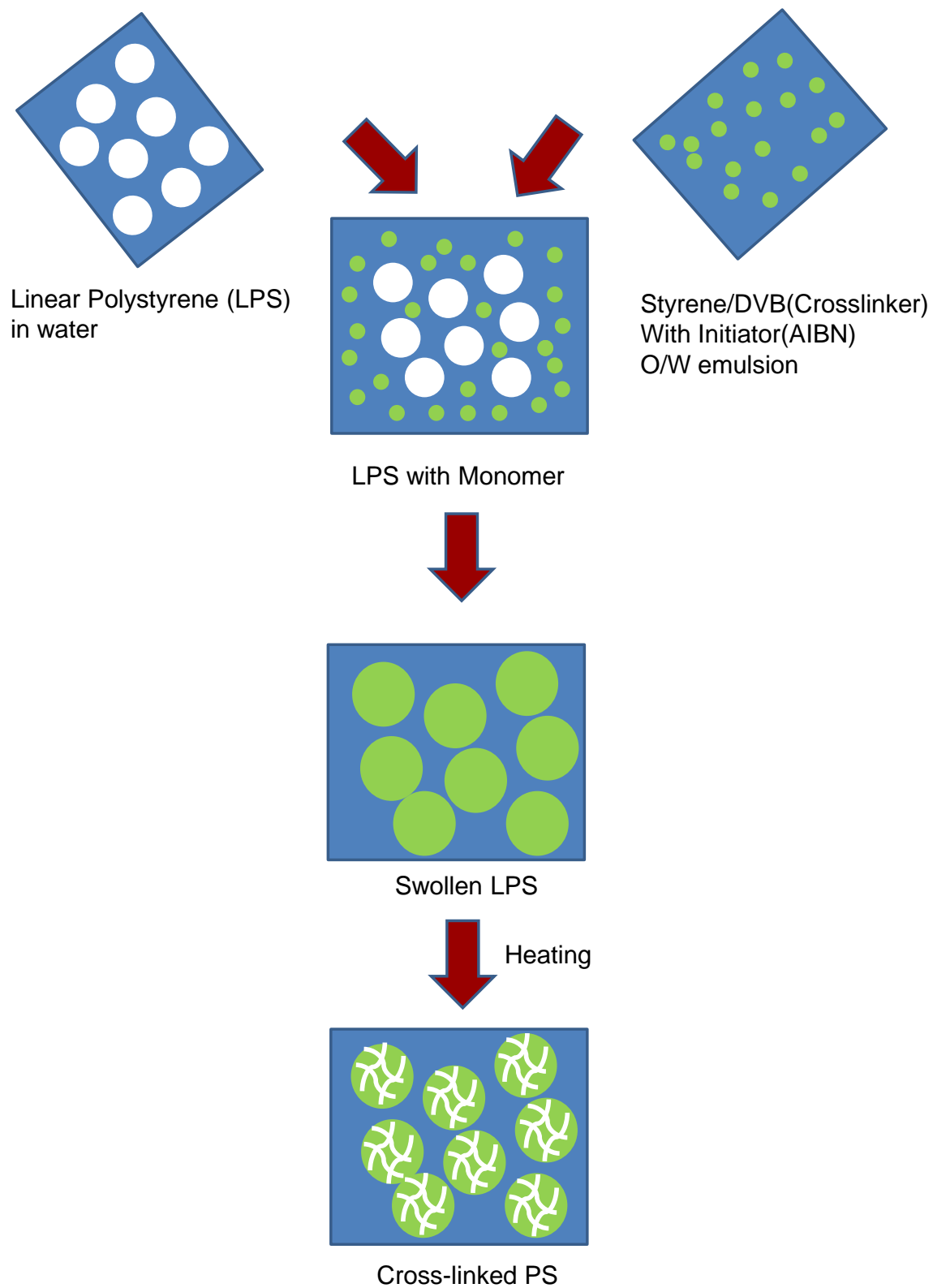


Figure 2.2: A typical procedure for Seeded Emulsion Polymerization.

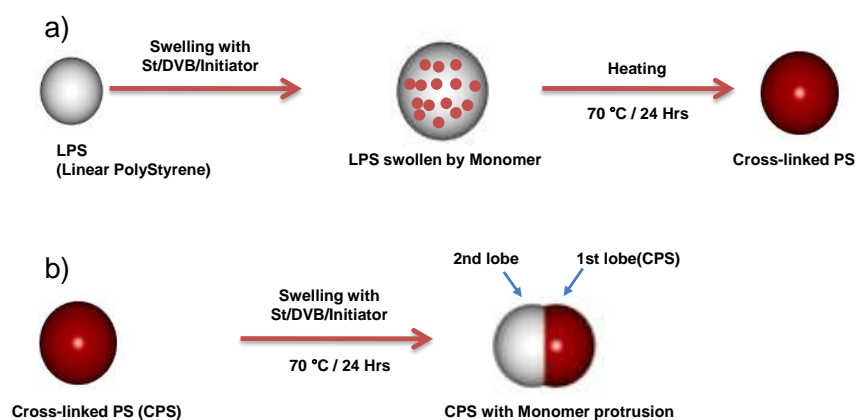


Figure 2.3: Synthetic scheme for Dimer particle whose size is greater than one micron
a) 1st Seeded Emulsion Polymerization; b) 2nd Seeded Emulsion Polymerization

We developed a modified seeded-emulsion polymerization by incorporating a silane-coupling agent to synthesize submicron-sized Dimer particles. Instead of cross-linked particles, the new synthetic method makes core-shell particle, which is the precursor for the submicron-sized Dimer particles. The shell of the particle is a copolymer consisting of the silane-coupling agent and styrene. The shell prefers to be separated from the core for entropic reason when it meets with styrene and thus the precursor transforms into Dimer particle upon swelling with styrene.

The new synthetic method consists of synthesis of Linear Polystyrene particles (LPS) and two seeded-emulsion polymerization as illustrated in Figure 2.4a. We use surfactant-free emulsion polymerization to synthesize monodisperse linear polystyrene (LPS) particles (Figure 2.4b). (Goodall, Wilkinson et al. 1977; Tauer, Deckwer et al. 1999) These particles serve as the seeds for the first seeded-emulsion polymerization. Linear polystyrene particles are stabilized by surface sulfate groups generated from a water soluble radical initiator, potassium persulfate. (Furusawa, Norde et al. 1972; Goodall, Wilkinson et al. 1977; Tauer, Deckwer et al. 1999) The typical diameter of the LPS particles obtained by surfactant-free emulsion polymerization is ~ 400 nm. In the first seeded-emulsion polymerization, the LPS particles are mixed with an oil-in-water (O/W) emulsion, where the oil phase is styrene,

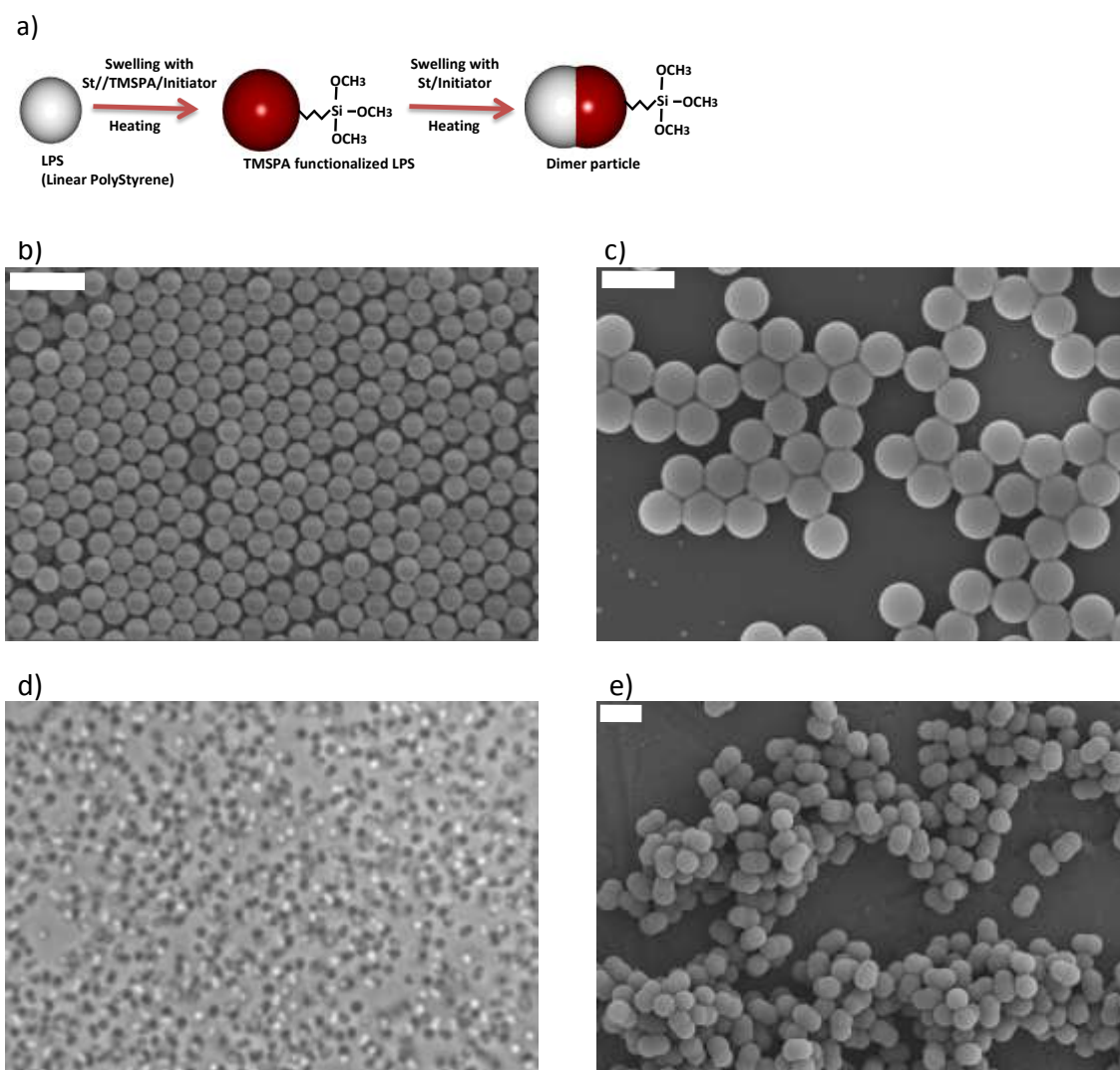


Figure 2.4: a) Schematic illustration showing the synthesis of submicron-sized Dimer particles. b) SEM image of seed particles obtained by surfactant emulsion polymerization. The scale bar represents 1 μ m. c) SEM image of TMSPA functionalized LPS. d) Optical microscope image (100X) of Dimeric particle shape right after swelling of monomer mixture. e) SEM image of Dimer particles. The scale bar represents 1 μ m.

2,2'-azodi(2,4'-dimethylvaleronitrile) (ADV N; initiator) and 3-(trimethoxysilyl) propyl acrylate (TMSPA). ADV N is a thermal initiator for free radical polymerization. ADV N was chosen as an initiator because it has the lowest solubility in water. Thus, ADV N hardly diffuses into water phase during the seeded-emulsion polymerization. Conventional initiators such as Azobisisobutyronitrile (AIBN) can diffuse into water and induces miniemulsion polymerization, which makes many unfavorable small particles. (Asua 2002)

The TMSPA contains an acrylate group, which copolymerizes with styrene. The TMSPA also contains tri-alkoxy silane, which provides reactive sites to enable further functionalization. (Kim, Lee et al. 2008) Upon mixing the LPS dispersion with the monomer emulsion, monomers diffuse into LPS particles and form monodisperse droplets. These swollen LPS droplets are converted to TMSPA-functionalized LPS particles by raising the temperature of the mixture to 70°C for 24 hrs (Figure 2.4c). The second seeded-emulsion polymerization is performed to obtain Dimer particles. The TMSPA functionalized LPS dispersion is mixed with an O/W emulsion. The oil phase of this emulsion contains styrene and ADV N but does not contain TMSPA. Upon mixing with the O/W emulsion, spherical TMSPA-functionalized LPS particles spontaneously transform into a Dimeric structure (Figure 2.4d). The shape and size of the Dimeric structure is highly uniform. These Dimeric structures have been reported to form from a

core-shell structure obtained from the seeded-emulsion polymerization.(Park, Forster et al. 2010) Styrene and LPS form the core which phase separates from the hydrophilic shell made of TMSPA-rich polystyrene copolymers. Polymerization to solidify the Dimeric structure is initiated by raising the temperature to 70 °C for 24 hrs (Figure 2.4e).

The size ratio of two lobes can be controlled by swelling amount of monomer during the 2nd seeded-emulsion polymerization (Figure 2.5).(Kim, Lee et al. 2008) The typical swelling ratio to give dumbbell-like Dimer particles is TMSPA-functionalized LPS : monomer = 1: 4 (figure 4e). Polyvinylalcohol (PVA) is used to make monomer emulsion because PVA can be easily washed away using methanol while removing molecular surfactants such as Sodiumdodecylsulfate (SDS) require dialysis. This synthetic method doesn't exploit cross-linked particles to make Dimer particles. TMSPA plays key role in forming Dimer particles. However, particles made by copolymerizing styrene with TMSPA can't be used as a precursor to make Dimer particles.(Park, Forster et al. 2010) TMSPA-functionalized particles made by seeded-emulsion polymerization have a unique core-shell structure and the shell separates into another lobe when the TMSPA-functionalized particles are swollen with styrene.

In this chapter, we presented a synthetic method to synthesize submicron-sized Dimer particles by modifying conventional seeded emulsion polymerization. The method

can produce monodisperse submicro-sized Dimer particles in a large quantity. However, in order to exploit the potential of the Dimer particles as an anisotropic building block, introducing the anisotropy in the surface properties is highly desired. Dimer particles would be more attractive non-spherical colloids if each lobe could be independently functionalized. We discovered that gold nanoparticles are very useful in asymmetrically

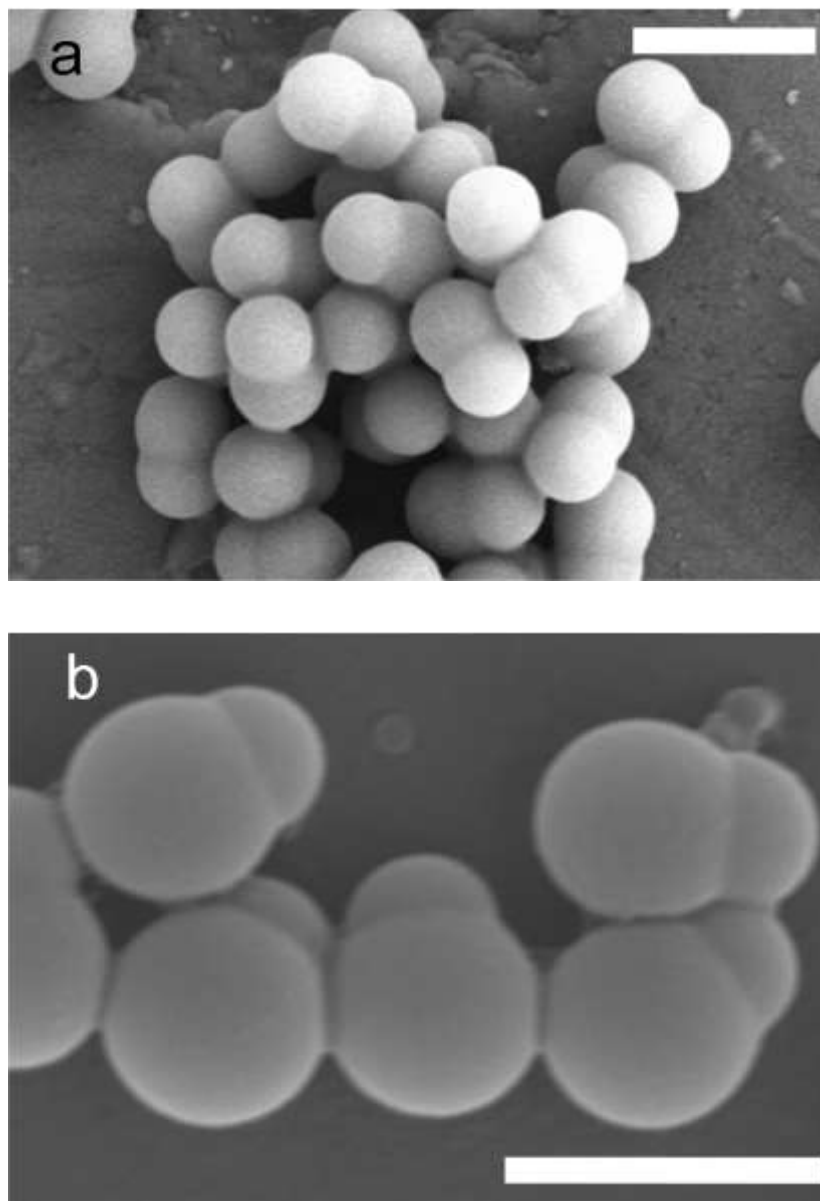


Figure 2.5: Submicron-sized Dimer particles with different swelling volume ratios a) monomer : TMSPA-functionalized LPS = 3 : 1. b) monomer : TMSPA-functionalized LPS = 2 : 1. The scale bar represents 1 μm .

functionalizing Dimer particles. Furthermore, gold nanoparticles can provide us with evidences for the suggested mechanism of Dimeric structure formation. Functionalizing Dimer particles with gold nanoparticles will be discussed in chapter 3.

2.3 Experimental Procedures

To synthesize LPS particles, we add 140 ml of deionized water, 10 ml of styrene and 22 mg of potassium persulfate into a one-neck rounded flask. The flask is sealed with rubber septum and purged with nitrogen. The flask is then placed in ultrasonication bath for ten minutes. Polymerization is performed by heating the flask to 75°C while it is tumbled at 30 RPM for 20 hours. After the polymerization, the reaction mixture is slowly cooled to room temperature. The diameter of LPS particles is ~380 nm determined by scanning electron microscopy. We then use the seeded emulsion polymerization technique for the synthesis of TMSPA-functionalized LPS. 0.5 g of LPS particles are redispersed in 2 ml of 2 w/v% polyvinylalcohol (PVA, 85~89% hydrolyzed, Mn 85,000~124,000 g·mol⁻¹, Sigma-Aldrich) aqueous solution. We prepare a monomer solution containing 1.6 ml of styrene (St, 99%, Sigma-Aldrich), 0.4 ml of 3-(trimethoxysilyl) propyl acrylate (TMSPA, Sigma-Aldrich) and 40 mg of thermal

initiator, 2,2'-azodi (2,4'-dimethylvaleronitrile) (V-65B,Wako). The monomer solution is emulsified in 8 ml of 2 w/v% PVA aqueous solution. The O/W emulsion is then mixed with the LPS seed particle dispersion and the mixture is tumbled at 40 rpm for 24 hours to allow the seed particles to be swollen by the monomer mixtures. Then, polymerization is carried out at 70°C for 24 hours and the tumbling speed is 60 rpm. The size of the TMSPA functionalized LPS particles increased by ~50 %. To make Dimer particles, 0.5 g of TMSPA functionalized LPS particles were swollen by monomers containing 2 ml of St and 40 mg of the thermal initiator using the same procedure described above. The monomer mixture for the second swelling does not contain TMSPA. Dimeric shape is observed before the polymerization is conducted. Polymerization is performed under the same conditions described for the synthesis of TMSPA functionalized LPS particles. After the polymerization, the Dimer particles are washed by methanol several times to remove PVA and unreacted monomers.

Chapter 3

Asymmetric functionalization of Dimer particles with gold nanoparticles

3.1 Introduction

Dimer particles have been used as building blocks to fabricate new photonic materials(Hosein and Liddell 2007; Hosein, Ghebrebrhan et al. 2009; Forster, Park et al. 2011), and other complex structures.(Kraft, Vlug et al. 2008; Kraft, Groenewold et al. 2009) They also have been studied as colloid surfactant for the stabilization of pickering emulsions.(Kim, Lee et al. 2008) To fully take advantage of the anisotropy of Dimer particles, it is highly desirable to develop methods to tailor the surface property of each lobe independently. The asymmetric functionalization of Dimer particles would expand their application as colloid surfactants, since the shape and surface anisotropies can be controlled independently, analogous to molecular surfactants such as diblock copolymers. The asymmetric surface functionalization of Dimer particles, however, has not been explored extensively. It has been shown that only one lobe of Dimer particles can be

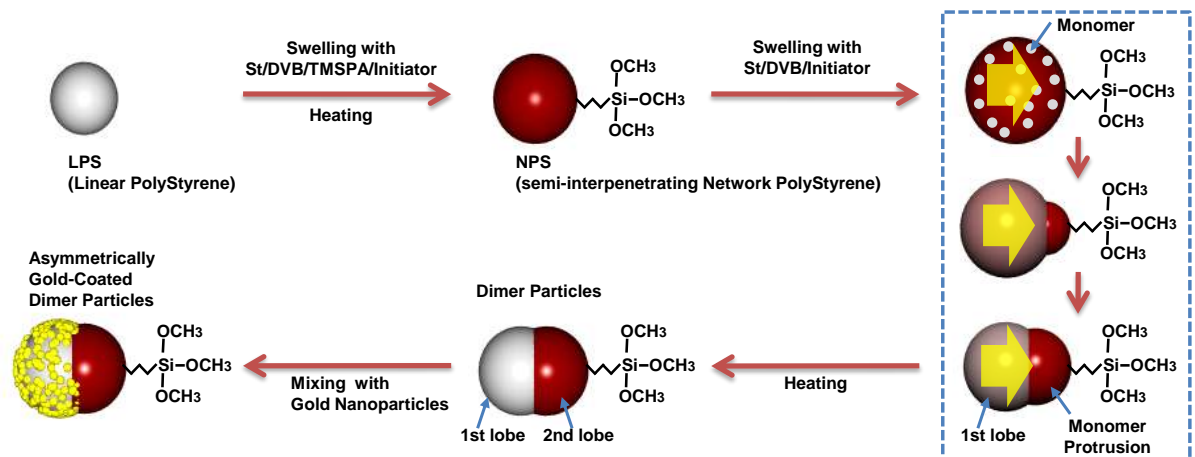
further functionalized.(Kim, Larsen et al. 2006; Kim, Lee et al. 2008) Other studies have shown that asymmetric functionalization of spherical colloids can be achieved by the selective deposition of a metal (e.g., gold) onto one hemisphere of particles.(Takei and Shimizu 1997; Paunov and Cayre 2004; Suzuki and Kawaguchi 2006) These approaches, however, require two-dimensional arrangement of particles at an interface, which is difficult to achieve with Dimer particles.(Fujimoto, Nakahama et al. 1999; Lu, Yin et al. 2001; Lu, Xiong et al. 2003)

Herein, we present a novel method to synthesize asymmetrically gold-coated Dimer particles and elucidate the particle's formation mechanism. This method doesn't need the arrangement of particles onto any type of interfaces. Asymmetric coating of gold nanoparticles can be carried out simply by mixing Dimer particles with gold nanoparticles. The Dimer particle has dumbbell-like shape and the gold nanoparticles selectively attach onto one lobe of the Dimer particles. The asymmetrically gold-coated Dimer particles are highly monodisperse and can be produced in large amount. Furthermore, the two surfaces of the asymmetrically gold-coated Dimer particles have distinct functional groups, which can be further tailored to have various sets of asymmetric surface properties.

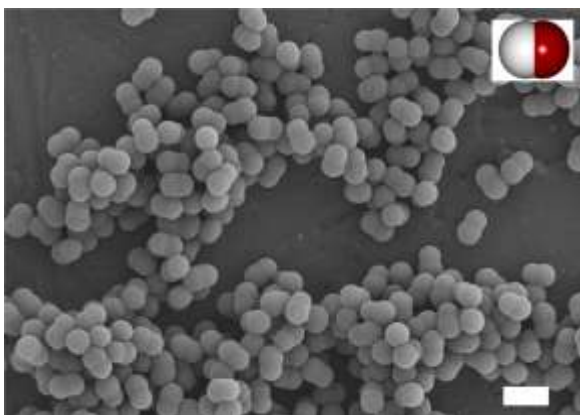
3.2 Results and Discussion

The synthesis of the asymmetrically gold-coated Dimer particles proceeds in four steps. Surfactant-free emulsion polymerization is followed by two sequential seeded-emulsion polymerization, and, subsequently, by the selective attachment of gold nanoparticles to one lobe of Dimer particles as illustrated in Figure 3.1. We use surfactant-free emulsion polymerization to synthesize monodisperse linear polystyrene (LPS) particles, which are the seeds for the first seeded-emulsion polymerization. LPS particles are stabilized by surface sulfate groups generated from the thermal initiator, potassium persulfate. The average diameter of LPS particles is ~ 380 nm. In the first seeded-emulsion polymerization, LPS particles are mixed with an oil-in-water emulsion, of which oil phase comprises styrene, divinylbenzene (DVB; crosslinker), 2,2'-azodi(2,4'-dimethylvaleronitrile) (ADV; initiator) and 3-(trimethoxysilyl) propyl acrylate (TMSPA) (Figure 3.1). TMSPA contains a vinyl group, which copolymerizes with styrene. TMSPA also contains tri-alkoxy silane, which provides functional groups to enable further functionalization⁵. Upon mixing the LPS dispersion with the monomer emulsion, monomers diffuse into LPS particles and form monodisperse droplets. These swollen LPS droplets are converted to semi-interpenetrating network polystyrene (NPS)

a)



b)



c)

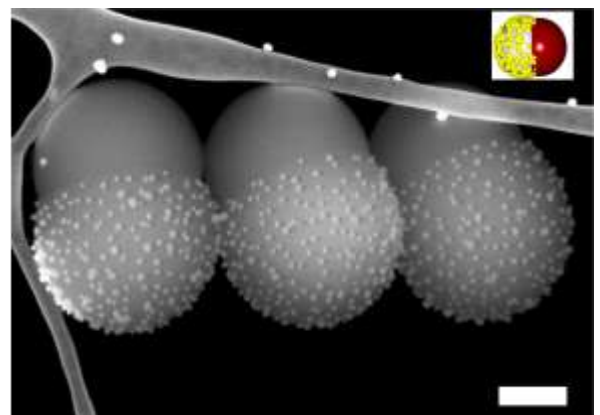


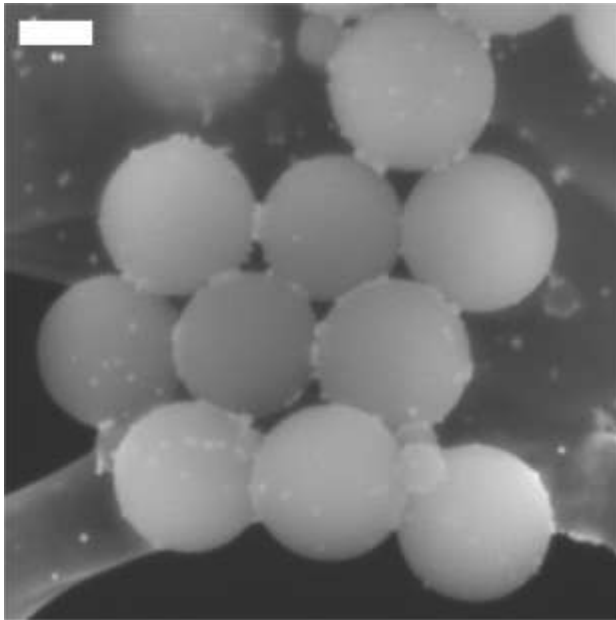
Figure 3.1: Synthesis of Dimer particles with asymmetric coating of gold nanoparticles.

a) Schematic representation of the synthesis. b) Electron Scanning Micrographs of Dimer particles. The scale bar represents 1 μ m. c) Dimer particles with asymmetric coating of gold nanoparticles. The Scale bar represents 200nm.

particles by raising the temperature of the mixture to 70°C for 24 hrs. The second seeded-emulsion polymerization is performed to obtain Dimer particles. The NPS dispersion is mixed with an oil-in-water emulsion. The oil phase of this emulsion contains styrene, DVB and ADVN but does not contain TMSPA. Upon mixing with the O/W emulsion, spherical NPS particles transform into Dimeric structure spontaneously. One lobe of these Dimer particles is polystyrene, whereas the other lobe comprises the monomer mixture. These Dimeric structures are formed due to the protrusion of the monomer mixture from the swollen NPS particles (Kraft, Vlug et al. 2008). Polymerization to solidify the second lobe is initiated by raising the temperature to 70 °C for 24 hrs. Finally, the addition of citrate-stabilized gold nanoparticles leads to the formation of asymmetrically gold-coated Dimer particles as seen in Figure 3.1(c). Ultrasonication does not detach gold nanoparticles from the Dimer particles, illustrating that the adhesion between the two particles is strong.

To verify which lobe of the Dimer particles has affinity to citrate-stabilized gold nanoparticles, we test the interactions of two types of NPS particles with citrate-stabilized gold nanoparticles: NPS particles with and without TMSPA. Gold nanoparticles do not show affinity to NPS particles with TMSPA, whereas gold nanoparticles adsorb favorably onto NPS particles without TMSPA as shown in Figure 3.2. TMSPA likely undergoes

a)



b)

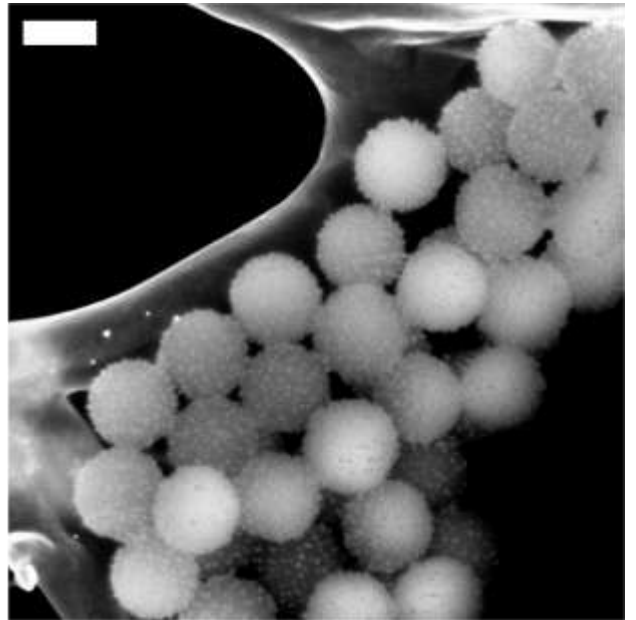


Figure 3.2: a) Electron Scanning Micrographs of NPS with TMSPA. The particles don't have affinity to gold nanoparticles. The scale bar represents 200nm. b) Electron Scanning Micrographs of NPS without TMSPA The particles show affinity to gold nanoparticles. The Scale bar represents 300nm.

hydrolysis during the synthesis, making the surface of NPS similar to that of silica particles(Perro, Meunier et al. 2009). It is well known that citrate-stabilized gold nanoparticles do not adsorb favorably onto silica surface due to electrostatic repulsions. We believe the binding of gold nanoparticles onto TMSPA-less NPS particles is driven by non-specific interactions such as van der Waals interaction and hydrophobic interaction between hydrophobic polystyrene surface and gold nanoparticles.

From these results, it seems natural to conclude that the lobe formed during the second seeded-emulsion polymerization has the affinity to gold nanoparticles because TMSPA is not present in the emulsion used for the second seeded-emulsion polymerization. However, we make an unexpected observation that indicates the opposite is true. By vigorously stirring the dispersion of NPS particles with monomer protrusion before the second-seeded polymerization, water molecule-like particles are generated due to the coalescence of two NPS particles with monomer protrusion (Figure 3.3a).(Kraft, Vlug et al. 2008; Park, Forster et al. 2009) The addition of gold nanoparticles to the suspension of these water molecule-like particles shows that gold nanoparticles adsorb selectively onto the two “hydrogen” lobes rather than to the “oxygen” lobe. (Figure 3.3b)

These observations lead us to hypothesize that the surface property of the first lobe changes drastically during the second seeded-emulsion polymerization. That is, the first

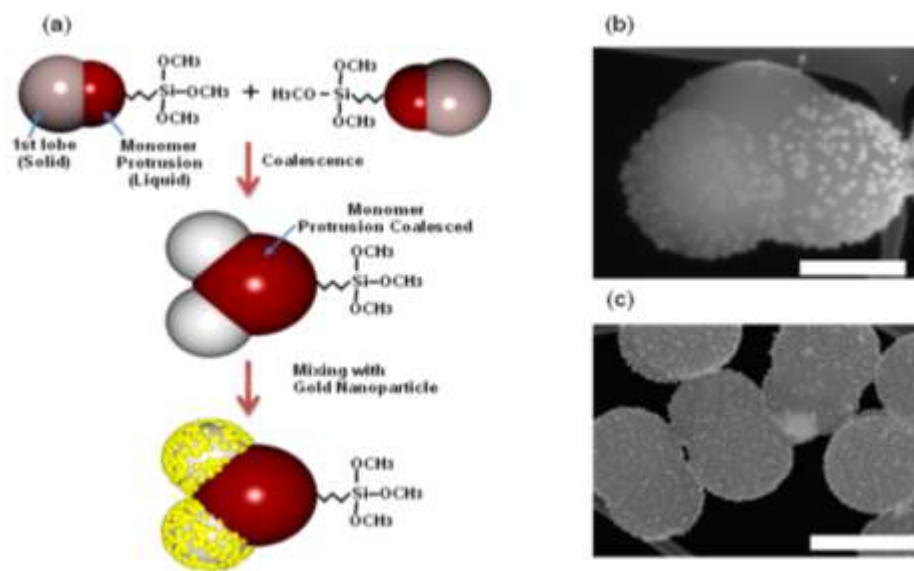
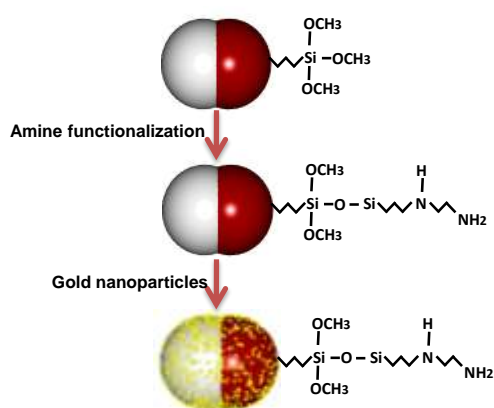


Figure 3.3: a) Schematic representation of the synthesis of water molecule-like particles using coalescence. The particles are mixed with gold nanoparticles. b) Electron Scanning Micrographs of Water molecule-like particles with gold nanoparticles. The scale bar represents 300nm. c) Electron Scanning Micrographs of partially-Amine-functionalized dimer particles with gold nanoparticles. The particles are fully covered by gold nanoparticles. The scale bar represents 500nm.

lobe does not completely inherit its property from NPS particles with TMSPA. We believe that TMSPA does not randomly copolymerize with styrene during the first seeded-emulsion polymerization, possibly due to the difference in the reactivity ratio.(O'dian 2004) TMSPA-rich polymers in the NPS particles migrate from the first lobe to the second lobe during the swelling stage before the second seeded-emulsion polymerization.(Figure 3.1a) The driving force of the migration is the free energy gain obtained by isolating TMSPA-rich polymer into the styrene monomer phase.(Flory 1953) TMSPA-rich polymer is more compatible with styrene monomer than it is with polystyrene. We confirm that the low compatibility of TMSPA with polystyrene indeed facilitates the protrusion of the monomer mixture and, in turn, the synthesis of Dimer particles. The absence of TMSPA in NPS particles prevents the formation of the monomer protrusion during the second seeded emulsion polymerization. The shape of swollen NPS particles without TMSPA is close to a sphere rather than dumbbell.

Our hypothesis is further supported by the formation of Dimer particles that are fully coated with gold nanoparticles. We functionalize Dimer particles with amine groups using an amino-silane-coupling agent, N-[3-(trimethoxysilyl)propyl] ethyleneamine (TMSPE, Sigma-Aldrich). This agent (TMSPE) reacts with TMSPA to impart amine functional groups onto the particle surface. This reaction, therefore, selectively converts

a)



b)

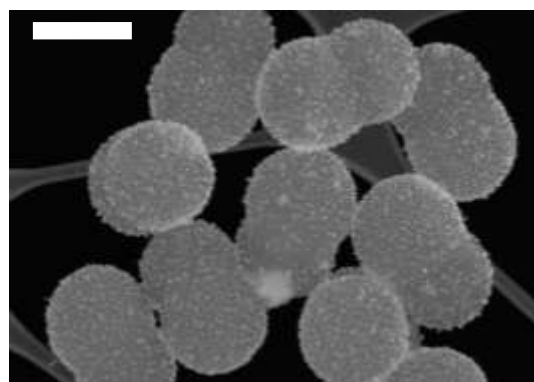


Figure 3.4: a) Schematic representation of the synthesis of amine functionalized dimer particles with gold nanoparticles. b) SEM image of amine functionalized dimer particles with gold nanoparticles. The scale bar represents 500nm.

TMSPA-functionalized surface to amine-functionalized surface. TMSPE-functionalized Dimer particles are subsequently mixed with citrate-stabilized gold nanoparticles. Remarkably, resulting Dimer particles have full coatings of gold nanoparticles on both sides of the Dimers as seen in Figure 3.4(b). Attractive interactions between amine groups and citrate-stabilized gold nanoparticles through electrostatic interactions is well known and widely exploited to induce the adsorption of gold nanoparticles onto silica surfaces⁴. Since TMSPA is not present in the monomer emulsion for the second seeded-emulsion polymerization, TMSPA on the surface of the second lobe most likely has been extracted from the NPS particles. The only possible step in which TMSPA could migrate from the first to the second lobes is the swelling of NPS particles with the monomer mixture during the second seeded-emulsion polymerization.

In this chapter, we presented a method to asymmetrically functionalize Dimer particles with gold nanoparticles. We have elucidated the mechanism of this selective functionalization and shown that the migration of TMSPA-rich polymers from the first lobe to the second one results in the asymmetric surface functionality of these Dimer particles. This solution-based synthetic approach is advantageous to other asymmetric functionalization methods because it does not require the use of vacuum based metal deposition for asymmetric functionalization of colloids. Therefore, our method enables

the fabrication of asymmetrically functionalized Dimer particles in a large scale. These asymmetrically functionalized Dimers are promising building blocks to generate suprastructures that will be useful in photonic, electronic and diagnostic applications.(Fudouzi and Xia 2003; Daniel and Astruc 2004; Yoshida and Lahann 2008)

3.3 Experimental Procedures

Asymmetrically coated Dimer particles are obtained simply by mixing Dimer particles with citrate-stabilized gold nanoparticles. Citrate-stabilized gold nanoparticles are prepared by the Turkevich method.(Daniel and Astruc 2004) Gold nanoparticles are produced by reduction of Chloroauric acid. After dissolving Chloauric acid, the solution is rapidly stirred while a reducing agent is added. Gold gradually starts to precipitate in the form of subnanometer particles. Excess amount of gold nanoparticles is added to the Dimer particles dispersed in methanol. The mixture is lightly stirred with a magnetic bar for three hours at room temperature. The mixture is then washed by methanol several times to remove residual gold nanoparticles. For the growth of gold nanoparticles, we prepare reducible gold salt solution by dissolving 10 mg of potassium carbonate (K_2CO_3) in 40ml of deionized water. 0.01 mg of Chloroauric acid ($HAuCl_4$,Sigma-Aldrich) and

age the solution in the dark for at least one day before use. A hydroxylamine hydrochloride($\text{NH}_2\text{OH}\cdot\text{HCl}$, Sigma-Aldrich) solution is prepared by adding 1.3 mg of hydroxylamine hydrochloride into 10 ml of deionized water. Then, 10 mg of asymmetrically gold-coated Dimer particles is dispersed in 1ml of deionized water. After adding 0.3ml of K_2CO_3 / HAuCl_4 solution, the mixture is sonicated for 10 min. Finally, 0.15 ml of hydroxylamine hydrochloride solution is added into the particle dispersion. There is a color change from red to violet. The dispersion is centrifuged and washed with deionized water.

Chapter 4

Assembly of Dimer particles using DC/AC electric field

4.1 Introduction

Extensive researches in colloid science have provided well-established techniques to synthesize monodisperse and stable spherical colloid particles. (Morfesis, Hagopian et al. 1988; Murray and Grier 1996; Caruso, Caruso et al. 1998; Reese, Guerrero et al. 2000; Bosma, Pathmamanoharan et al. 2002; Peng, van der Wee et al. 2012) In recent years, there have been approaches to push the application boundaries of colloid science by exploiting non-spherical colloids for self assembly (Liu, Nie et al. 2010; Chen, Bae et al. 2011; Henzie, Grunwald et al. 2012) and external-field-directed assembly. (Gangwal, Cayre et al. 2008; Gangwal, Cayre et al. 2008; Velev, Gangwal et al. 2009; Demirors, Johnson et al. 2010; Forster, Park et al. 2011; Kretzschmar and Song 2011) For instance, researches of assembling Dimer particles using induced dipole-dipole interactions from electric fields have been conducted. (Demirors, Johnson et al. 2010; Forster, Park et al.

2011) Along with the induced dipole-dipole interactions from electric fields, electrohydrodynamic interactions and dipole-field interaction can play an important role in external-field-directed assembly of Dimer particles. However, systematic investigations of external-field-directed assembly of Dimer particles considering all the above interactions have not been conducted.

In this chapter, we investigate the assembling behavior of Dimer particles under DC and AC field. We show that sophisticated balancing among dipole-dipole interaction, electrohydrodynamic interaction, and dipole-field interaction can control the orientation and assembly of Dimer particles. Close-packed crystals of standing Dimer particles can be obtained by adjusting the history of frequency change. The rich phase behavior of Dimer particles is demonstrated by changing the frequency of AC field. The phases have different orientations of Dimer particles inside and outside of the assembly. The formation of each phase is explained by carefully considering the interactions involved in the AC field system.

4.2 Results and Discussion

Figure 4.1 illustrates the experimental setup for the electric-field-directed assembly

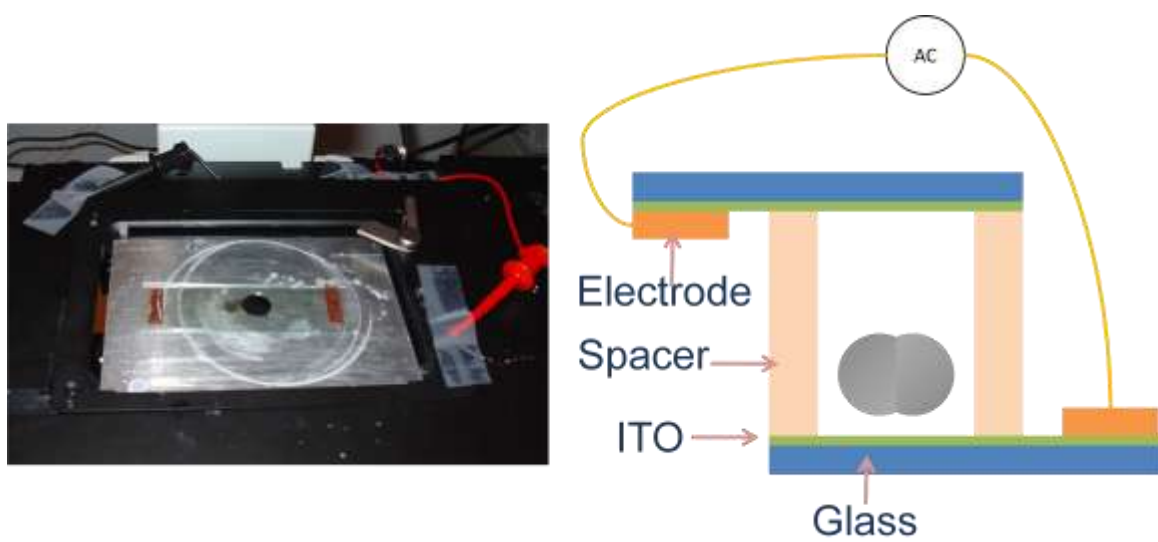


Figure 4.1: Schematic representation of the experimental setup for field-directed assembly of Dimer particles

of Dimer particles. Two conducting indium-tin-oxide (ITO) glasses were used with spacers. The ITO glass itself is an electrode and the electric field is perpendicular to the ITO glasses. Dimer particles are placed inside the slab and exposed to the following interactions under DC and AC electric field: induced dipole-dipole interaction, two electrohydrodynamic interactions from equilibrium-charge electroosmotic (ECEO) flow and induced-charge electroosmotic (ICEO) flow, and dipole-field interaction.

The dipole moment induced by an electric field E is described as $p = \alpha E$, where α is the polarizability of the particle. The polarizability is a function of permittivities, bulk conductivities of both particle and dispersion media, and surface conductivity of the particle.(Jones 1995) An induced dipole-dipole interaction from two particles aligned perpendicular to the electric field is repulsive as described in the equation 1

$$U_{dd} = \frac{1}{4\pi\epsilon_0\epsilon_r} \frac{p_1 p_2}{r^3}$$

,where ϵ_r and ϵ_0 is the dielectric constant of the dispersion media and vacuum respectively, and r represents the separation distance between the two particles. The assembly can occur when the repulsive induced dipole-dipole interaction is exceeded by attractive interactions from equilibrium-charge electroosmotic (ECEO) flow along the surface of the particles under DC field.(Prieve, Sides et al. 2010) Under AC fields,

induced-charge electroosmotic (ICEC) flow becomes more important. ICEC flow occurs around the polarizable layer of electrodes. The particles on the conducting substrate perturb the electric field normal to the substrate and generate tangential electric field components along the substrate. The tangential electric field acts on the excess surface charges on the polarization layer and consequently generate electroosmotic flows.(Jones 1995; Solomentsev, Bohmer et al. 1997; Ristenpart, Aksay et al. 2004; Prieve, Sides et al. 2010)

In addition to the electrohydrodynamic interactions from ECEO and ICEO flow, Dimer particles are subject to an electric torque from dipole-field interaction. It is energetically favorable for Dimer particles to be aligned with one of its principle axes of the electric field. Dimer particles can be approximated to ellipsoids and the dipole-field interaction energy is

—

,where α and β are parallel and perdicular polarizabilities repectively.(Jones 1995) The a and b represent the length of ellipsoids, and θ is the angle between an electric field and major axis of an ellipsoid. If the ellipsoid's major axis is parallel with the electric field, θ is 90°. Thus, the free energy can be minimized by making Dimer particles stand up(if α is greater than

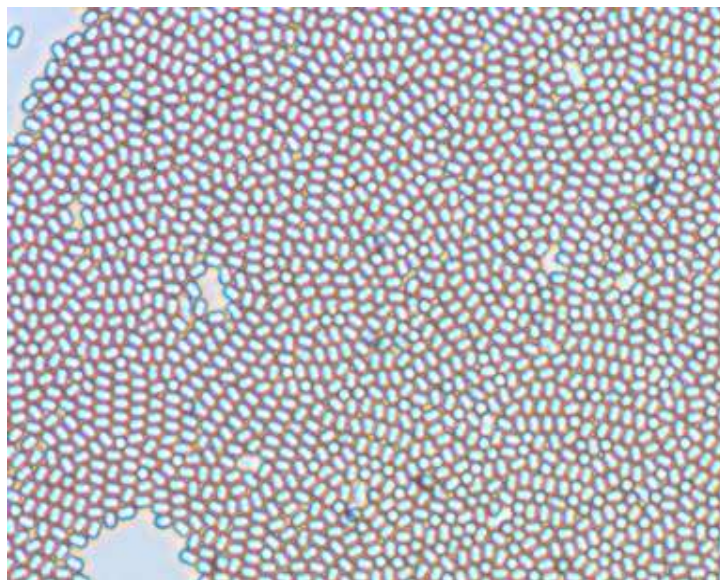


Figure 4.2: Assembly of Dimer particles under a DC electric field

.(Saville, Bellini et al. 2000)

We first observed Dimer particles with DC electric field, where the bottom substrate has positive charges. Since the Dimer particles have negative charges, the particles move toward the bottom substrate when the DC electric field is turned on. As the voltage reaches ~2.1V, the Dimer particles start to assemble at the bottom of the substrate as shown in Figure 4.2. If the bottom substrate's charge changes from negative to positive, the Dimer particles dissemble. Thus, the DC-field-directed assembly of Dimer particles are consistent with spherical particles assembly by equilibrium-charge electroosmotic flow on the substrate.(Prieve, Sides et al. 2010) The velocity of equilibrium-charge electroosmotic flow is

Where, η is the viscosity of solvent and ζ is the zeta potential of colloids. The velocity decreases as the salt concentration increases due to the reduced zeta potential of particles. When the salt concentration reaches a threshold, the Dimer particles don't assemble under the DC field anymore. A typical threshold salt concentration is 10 mM.

Dimer particles show more interesting behaviors under AC field. Figure 4.3 shows close-packed standing Dimer particles under AC field. The crystal is nearly perfect and almost all Dimer particles stand up and assemble to ordered structures. The assembly is

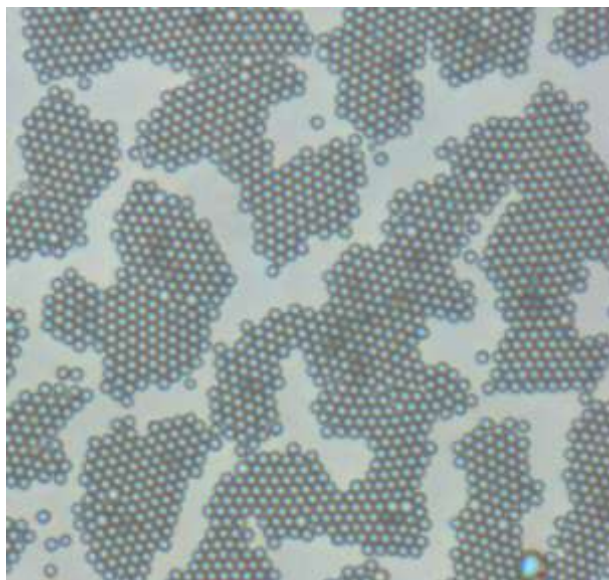


Figure 4.3: 2D close-packed structure with standing Dimer particles under an AC electric field

achieved by two steps. Firstly, the AC field is turned on with the frequency of $\sim 10,000\text{Hz}$. At this frequency, Dimer particles are aligned to the normal electric field due to the electric torque. The frequency is then gradually decreased so that the electroosmotic flow starts working on Dimer particles and assembling them. This two-step process is reversible in that the Dimer particles are redispersed when the electric field is turned off and reassemble when the electric field is applied by the two steps.

Phase behavior of Dimer particles at different field strengths, frequencies, and salt concentrations also has been studied. Phase behavior is strongly dependent on the frequency, but no strong dependence on field strength or salt concentration has been observed. The frequency change has changed increasing direction or decreasing direction. Dimer particles can take any orientations when they are far from the substrate. When they are close to the substrate, their orientations are parallel to the substrate due to the image charges in the conducting substrate. We denominate the low to high frequency path as path 1. At the beginning of path 1, Dimer particles aggregate while holding orientations parallel to the substrate. They then stand up when they meet each other and form an aggregate. This phase is named as “S-L”, where the former letter represents “standing orientation” inside the aggregates and the latter represents “lying orientation” outside the aggregates. When we increase the frequency further, L-L phase has been observed. In this

regime, ICEO flow is dominant to cause the horizontal arrangement of Dimer particles. Above $\sim 1.5\text{kHz}$, L-S phase is observed because the electric torque becomes significant to make Dimer particles stand up. Dimer particles are still parallel with the substrate inside the aggregate because ICEO flow is still strong in the regime around the substrate. As the ICEO flow is inversely proportional to frequency, Dimer particles start to be redispersed while maintaining the standing orientation as we increase the frequency further. ICEO is no longer strong enough to overcome the repulsive dipole-dipole interactions at high frequency.

Path 2, which is changing the frequency from high to low, reveals a different phase behavior. When the frequency is above $\sim 6000\text{Hz}$, standing Dimer particles are away from each other. As ICEO flow is sufficient enough by decreasing the frequency below 6000Hz , standing Dimer particles start to be close-packed. In this regime, the electric torque is strong enough to make Dimer particles stand up and ICEO is strong enough to assemble them into close-packed structures. Thus this phase is S-S phase. As expected, decreasing frequency generates S/L-S phase because ICEO becomes dominant to make Dimer particles change the orientation from standing to lying. Finally, L-L phase is reached by decreasing the frequency further. We also observed that the field strength has little effect on the positions of phase boundaries if it is strong enough. (e.g. 2V for

100micron slab)

Herein, we investigated electric-field driven assembly of Dimer particles. Due to the anisotropic geometry, Dimer particles shows rich phase behavior under electric field compared to spherical colloids. We also showed that we could generate the various phases by carefully designing the frequency curves parametrized by time. For example, 2-dimensional close-packed structures with standing Dimer particles can be obtained by starting from high frequency and gradually lower the frequency where both ICEO and electric torque is sufficient. We also have qualitatively analyzed the formation of each phase with four involving interactions: induced dipole-dipole interaction, ECEO, ICEO, and electric torque. The close-packed structure of Dimer particles has a potential as 3D fabrication of photonic crystals and this research will extend the possible superstructures made from anisotropic building blocks.

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